Chapter 6

Principles of Mass Transfer

Chapter 6 illustrates different situations where the third fundamental transfer process, *mass transfer*, is occurring in fuel cells or in the chemical processes to produce fuel for fuel cells. The following examples explain in detail how the flux of different species is affecting the performance of fuel cells.

6.1-1 Molecular Diffusion of Water in Air at the Cathode of a Fuel Cell
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6.3-1 Diffusion of Methanol in Water in Direct Methanol Fuel Cells
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6.5-1 Diffusion of Hydrogen through Nafion
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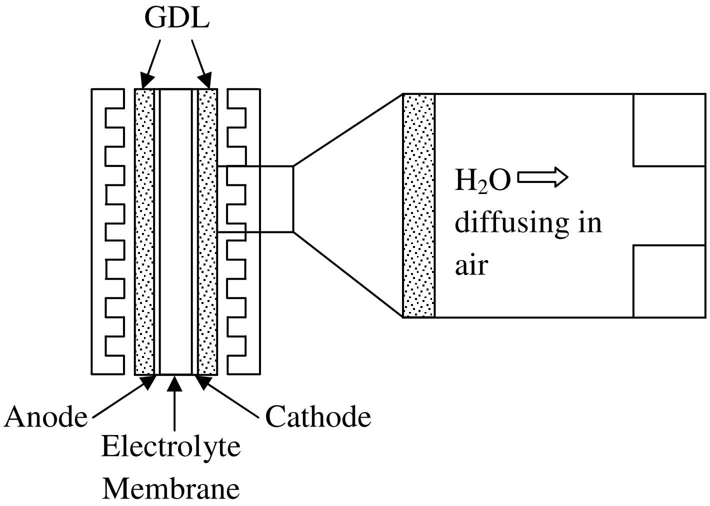
Example 6.1-1: Molecular Diffusion of Water in Air at the Cathode of a Fuel Cell

Proton – Exchange Membrane Fuel Cells consume hydrogen and oxygen from air to generate electricity, with heat and steam as byproducts. The steam being produced in the cathode side has a partial pressure of 0.22 bar. Some of the steam stays inside the fuel cell to keep the polymer – electrolyte membrane at an adequate humidity. The steam in the bipolar plate channels has a partial pressure of 0.024 bar. The distance between the gas diffusion layer (GDL) and the bipolar plate is 0.729 mm. Determine the diffusive flux from the gas diffusion layer to the bipolar plates of water in the air. The fuel cell is operating at a pressure and temperature of 2 bar and 40°C, respectively.

The following schematic illustrates the diffusion process taking place in the fuel cell:



Strategy

We can use Fick's law of diffusion to determine the steam flux through the air.

Solution

The equation that describes the flux of a chemical species due to diffusion is Fick's Law, given by:

$$J^*_{Az} = -D_{AB}\frac{dC_A}{dz}$$

This equation can be separated and integrated to yield:

$$J^*_{Az}\int_{z_1}^{z_2} dz = \underline{\hspace{8cm}}$$

$$J^*_{Az} = \underline{\hspace{6cm}}$$

The point where the steam is being produced will be considered $z_1 = 0$, whereas $z_2 = 0.729$ mm, since the outlet point is 0.729 mm away. The concentrations of the steam C_{A_2} and C_{A_1} will be determined from the ideal gas law, because the fuel cell is operating at relatively low pressure. Thus,

$$C_{A_1} = \frac{P_{A_1}}{RT} \qquad\qquad C_{A_2} = \frac{P_{A_2}}{RT}$$

Substituting the partial pressures, temperature and ideal gas constant into these equations, we have:

$$C_{A_1} = \frac{0.22 \text{ bar}}{\left(\underline{\qquad\qquad\qquad} \dfrac{\text{bar}\cdot\text{m}^3}{\text{mol}\cdot\text{K}}\right)(313.15 \text{ K})} = \underline{\qquad\quad} \frac{\text{mol}}{\text{m}^3}$$

$$C_{A_2} = \frac{0.024 \text{ bar}}{\left(\underline{\qquad\qquad\qquad} \dfrac{\text{bar}\cdot\text{m}^3}{\text{mol}\cdot\text{K}}\right)(313.15 \text{ K})} = \underline{\qquad\quad} \frac{\text{mol}}{\text{m}^3}$$

Now we can enter the concentrations we calculated into Fick's law to obtain the flux of steam, as shown below:

$$J^*_{Az} = \underline{\qquad\qquad\qquad} \frac{\text{m}^2}{\text{s}} \left[\frac{\underline{\qquad\quad} \dfrac{\text{mol}}{\text{m}^3} - \underline{\qquad\quad} \dfrac{\text{mol}}{\text{m}^3}}{(0.729 \text{ mm} - 0 \text{ mm})\left(\dfrac{1 \text{ m}}{1000 \text{ mm}}\right)} \right]$$

$$\boxed{J^*_{Az} = \underline{\qquad\quad} \frac{\text{mol}}{\text{m}^2\cdot\text{s}}}$$

The diffusivity value was obtained from Table 6.2-1 at a temperature of 42°C, which is relatively close to the operating temperature of 40°C.

Example 6.2-1: Equimolar Counterdiffusion at the Cathode Chamber of a Proton – Exchange Membrane Fuel Cell

In the diffusion process illustrated in Example 6.1-1, we calculated the flux of water in a fuel cell. For the same fuel cell, determine the flux of air diffusing in the steam.

Strategy

In a similar way to example 6.1-1 this problem can be solved using Fick's Law of Diffusion.

Solution

Since we need to determine the flux of air in the steam, we can start from Fick's Law. Thus,

$$J^{*}_{Bz} = \underline{\hspace{4cm}}$$

We can separate and integrate this equation to get:

$$J^{*}_{Bz}\left(\underline{\hspace{3.5cm}}\right) = -D_{BA}\left(\underline{\hspace{3.5cm}}\right)$$

$$J^{*}_{Bz} = \underline{\hspace{5.5cm}}$$

Since the pressure of the system is low, we can use Ideal Gas Law equation of state to calculate the pressures of air, as shown in the following equations:

$$C_{B_1} = \frac{P_{B_1}}{RT} \qquad\qquad C_{B_2} = \frac{P_{B_2}}{RT}$$

We can substitute these equations into Fick's Law equation to yield:

$$J^{*}_{Bz} = D_{BA}\left[\frac{\underline{\hspace{5cm}}}{RT(z_2 - z_1)}\right]$$

Since there is only air and steam in the cathode chamber of the fuel cell, we can calculate the partial pressures of air from Dalton's Law, which states:

$$P = \sum P_i$$

where:

P = Absolute pressure of the system

P_i = Partial pressure of component i in the gas mixture

Applying this equation for the number of gases in this problem and solving for the partial pressure of air, we have:

$$P = P_A + P_B$$

$$P_B = P - P_A$$

Substituting this equation into Fick's law, gives:

$$J^*_{Bz} = D_{BA}\left[\frac{\underline{\hspace{3cm}} - \underline{\hspace{3cm}}}{RT\left(z_2 - z_1\right)}\right] = D_{BA}\left[\frac{\underline{\hspace{5cm}}}{RT\left(z_2 - z_1\right)}\right]$$

Now we can enter the corresponding quantities into this equation to obtain the solution to this problem:

$$J^*_{Bz} = \left(2.88\times10^{-5}\ \frac{m^2}{s}\right)\frac{\underline{\hspace{2cm}}\ \text{bar} - \underline{\hspace{2cm}}\ \text{bar}}{\left(\underline{\hspace{4cm}}\ \frac{\text{bar}\cdot m^3}{\text{mol}\cdot K}\right)\left(313.15\ K\right)\left(\underline{\hspace{3cm}}\ m\right)}$$

$$\boxed{J^*_{Bz} = \underline{\hspace{3cm}}\ \frac{\text{mol}}{m^2\cdot s}}$$

The negative in this result indicates that the flux is going from point 2 (outlet stream) to point 1 (steam generation).

Example 6.2-5: Diffusion in Steam – Methane Reforming Process

Hydrogen for Proton – Exchange Membrane Fuel Cells is being produced from natural gas in a Steam – Methane Reforming Process. The natural gas reacts with steam to produce a mixture of Hydrogen and Carbon Monoxide, known as synthesis gas at a pressure of 20.45 atm and a temperature of 850°C. Determine the diffusivity of hydrogen in CO at these conditions using the Fuller method.

Strategy

We can obtain the diffusivity using Fuller method given in Section 6.2E of Geankoplis.

Solution

The diffusivity of a gas mixture can be calculated using the following equation:

$$D_{AB} = \frac{1\times10^{-7}T^{1.75}\left(\frac{1}{M_A}+\frac{1}{M_B}\right)^{1/2}}{P\left[\left(\sum\upsilon_A\right)^{1/3}+\left(\sum\upsilon_B\right)^{1/3}\right]^2}$$

For this problem we will select A = hydrogen, and B = carbon monoxide

The atomic diffusion volumes of hydrogen and carbon monoxide can be obtained from Table 6.2-2 of Geankoplis. Hence,

$$\sum\upsilon_A = 7.07$$

$$\sum\upsilon_B = \underline{\hspace{3em}}$$

We can substitute the process conditions, as well as the molecular weights and volumes of the gas species into the equation for D_{AB} to get:

$$D_{AB} = \frac{1\times10^{-7}\left(1123.15\,\text{K}\right)^{1.75}\left(\frac{1}{\underline{\hspace{3em}}}+\frac{1}{28}\right)^{1/2}}{\underline{\hspace{3em}}\ \text{atm}\left[\left(7.07\right)^{1/3}+\left(\underline{\hspace{3em}}\right)^{1/3}\right]^2}$$

$$\boxed{D_{AB} = \underline{\hspace{6em}}\ \frac{\text{m}^2}{\text{s}}}$$

Example 6.3-1: Diffusion of Methanol in Water in Direct Methanol Fuel Cells

Direct – methanol fuel cells are a type of fuel cells used for portable devices such as laptops and cell phones. The concentration of the methanol solution at the bottom of the reservoir is 32 wt. %. At the top of the tank, located 2 inches away, the concentration is 40 wt. %. Determine the diffusive flux of methanol in water at steady state at a temperature of 15°C. The densities of these two solutions at this temperature are $950.6\frac{\text{kg}}{\text{m}^3}$ for 32 wt. % CH_3OH at the bottom of the tank and $937.2\frac{\text{kg}}{\text{m}^3}$ for 40 wt. % CH_3OH at the top.

Strategy

The flux of methanol required in this problem can be calculated using the equation for flux of liquids at steady state, given in Section 6.3B of Geankoplis.

Solution

The equation for N_A for liquid mixtures is given by Equation 6.3-3 of Geankoplis.

$$N_A = \frac{D_{AB}C_{av}}{\underline{\qquad\qquad\qquad}}\left(x_{A_1} - x_{A_2}\right)$$

The diffusivity of methanol in water can be obtained from Table 6.3-1 of Geankoplis to be:

$$D_{AB} = \underline{\qquad\qquad\qquad}\ \frac{\text{m}^2}{\text{s}}$$

The average concentration of methanol can be obtained from the density and molecular weight of the methanol solution at both concentrations, as shown below:

$$C_{av} = \frac{\frac{\rho_1}{M_1} + \frac{\rho_2}{M_2}}{2}$$

To calculate the molecular weights at points 1 and 2, we use the following equation:

$$M_1 = \frac{100\text{kg}}{\frac{\text{wt.\% A @ point 1}}{M_A} + \frac{\text{wt.\% B @ point 1}}{M_B}} = \frac{100\text{kg}}{\left(\frac{32}{32} + \frac{68}{18}\right)\text{kgmol}} = \underline{\qquad\qquad}\ \frac{\text{kg}}{\text{kgmol}}$$

$$M_2 = \frac{100\text{kg}}{\frac{\text{wt.\% A @ point 2}}{M_A} + \frac{\text{wt.\% B @ point 2}}{M_B}} = \frac{100\text{kg}}{\left(\frac{\underline{\qquad}}{32} + \frac{\underline{\qquad}}{\underline{\qquad}}\right)\text{kgmol}} = \underline{\qquad\qquad}\ \frac{\text{kg}}{\text{kgmol}}$$

Now we can substitute the molecular weights to obtain the average concentration:

$$C_{av} = \frac{\dfrac{950.6\,\dfrac{\text{kg}}{\text{m}^3}}{\underline{\hspace{2cm}}\,\dfrac{\text{kg}}{\text{kgmol}}} + \dfrac{937.2\,\dfrac{\text{kg}}{\text{m}^3}}{\underline{\hspace{2cm}}\,\dfrac{\text{kg}}{\text{kgmol}}}}{2} = \underline{\hspace{2cm}}\,\frac{\text{kgmol}}{\text{m}^3}$$

The remaining unknowns are the molar fractions of methanol at points 1 and 2, and the average molar fraction of water in the tank. This can be done as follows:

$$x_{A_1} = \frac{\dfrac{\text{wt.\% A @ point 1}}{M_A}}{\dfrac{\text{wt.\% A @ point 1}}{M_A} + \dfrac{\text{wt.\% B @ point 1}}{M_B}}$$

$$x_{A_2} = \frac{\dfrac{\underline{\hspace{5cm}}}{\underline{\hspace{2cm}}}}{\dfrac{\text{wt.\% A @ point 2}}{\underline{\hspace{2cm}}} + \dfrac{\text{wt.\% B @ point 2}}{M_B}}$$

$$x_{BM} = \frac{x_{B_1} + x_{B_2}}{2} = \frac{(1 - x_{A_1}) + (\underline{\hspace{2.5cm}})}{2}$$

Notice that the average molar fraction of B was written in terms of x_{A_1} and x_{A_2}, since only methanol and water are present in the reservoir. Substituting the weight fractions and molecular weights into these equations yields:

$$x_{A_1} = \frac{\dfrac{\underline{\hspace{2cm}}}{32}}{\dfrac{\underline{\hspace{2cm}}}{32} + \dfrac{68}{\underline{\hspace{2cm}}}} = \underline{\hspace{2cm}}$$

$$x_{A_2} = \frac{\dfrac{\underline{\hspace{2cm}}}{\underline{\hspace{2cm}}}}{\dfrac{40}{\underline{\hspace{2cm}}} + \dfrac{60}{\underline{\hspace{2cm}}}} = \underline{\hspace{2cm}}$$

$$x_{BM} = \frac{(\underline{\hspace{2.5cm}}) + (\underline{\hspace{2.5cm}})}{2} = \underline{\hspace{2cm}}$$

We can now enter the values we calculated into the equation for the flux of A to get:

$$N_A = \frac{1.26\times10^{-9}\ \frac{\text{m}^2}{\text{s}}\left(\underline{\hspace{2cm}}\ \frac{\text{kgmol}}{\text{m}^3}\right)}{\left(0-2\ \text{in}\right)\left(\frac{0.0254\ \text{m}}{1\ \text{in}}\right)\left(\underline{\hspace{2cm}}\right)}\left(\underline{\hspace{2cm}}-\underline{\hspace{2cm}}\right)$$

As we can see in this equation, point 1 is at z = 2 in and point 2 is at z = 0, thus:

$$N_A = \frac{1.26\times10^{-9}\ \frac{\text{m}^2}{\text{s}}\left(\underline{\hspace{2cm}}\ \frac{\text{kgmol}}{\text{m}^3}\right)}{\left(-2\ \text{in}\right)\left(\frac{0.0254\ \text{m}}{1\ \text{in}}\right)\left(\underline{\hspace{2cm}}\right)}\left(\underline{\hspace{2cm}}-\underline{\hspace{2cm}}\right)$$

$$\boxed{N_A = \underline{\hspace{5cm}}\ \frac{\text{kgmol}}{\text{m}^2\cdot\text{s}}}$$

Example 6.3-2: Prediction of Diffusivity of Methanol in Water

Determine the diffusion coefficient of methanol in water using the Wilke – Chang equation at 15 °C. How does this value compare to the experimental diffusion coefficient in Table 6.3-1? Also calculate the diffusion coefficient of methanol in water at the operating temperature of Direct – Methanol Fuel Cells of 50°C.

Strategy

Wilke – Chang equation predicts the diffusivity of liquid mixtures, therefore, it can be used to calculate the diffusion coefficient of methanol in water at a given temperature.

Solution

Wilke – Chang equation is given in Section 6.3D of Geankoplis:

$$D_{AB} = 1.173\times10^{-16}\left(\phi M_B\right)^{1/2}\frac{T}{\mu_B V_A^{\,0.6}}$$

where:

ϕ = Association parameter of the solvent = 2.6 (This value is given for water in Section 6.3D)

M_B = Molecular weight of the solvent

μ_B = Viscosity of the solvent in $\mathrm{Pa\cdot s}$

V_A = Molar volume of the solute at the boiling point (Calculated using values from Table 6.3-2)

First we can calculate the molar volume of methanol. Since the molecular formula is CH_3OH, the molar volume is calculated as follows:

$$V_A = 1\left(\underline{\hspace{2cm}}\frac{m^3}{kgmol}\right) + 4\left(\underline{\hspace{2cm}}\frac{m^3}{kgmol}\right) + 1\left(0.0074\frac{m^3}{kgmol}\right)$$

$$V_A = \underline{\hspace{2cm}}\frac{m^3}{kgmol}$$

Substituting the rest of the parameters into Wilke – Change equation, we have:

$$D_{AB} = 1.173\times10^{-16}\left[2.6(\underline{\hspace{1.2cm}})\right]^{1/2}\left[\frac{288.15}{(\underline{\hspace{2.5cm}})(\underline{\hspace{2.5cm}})^{0.6}}\right]$$

$$\boxed{D_{AB} = \underline{\hspace{4cm}}\ \frac{m^2}{s}}$$

The viscosity for water was obtained from Appendix A.2 of Geankoplis at 15°C. We can observe this diffusivity value is relatively close to the experimental value in Table 6.3-1 of $1.26\times10^{-9}\ \frac{m^2}{s}$.

We can repeat this procedure to determine the diffusivity of methanol in water at the operating temperature of direct – methanol fuel cells. Again, the viscosity of water was obtained from Appendix A.2 at the temperature of 50°C.

$$D_{AB} = 1.173\times10^{-16}\left[2.6(18)\right]^{1/2}\left[\frac{323.15}{(\underline{\hspace{4cm}})(\underline{\hspace{3cm}})^{0.6}}\right]$$

$$\boxed{D_{AB} = \underline{\hspace{4.5cm}}\ \frac{m^2}{s}}$$

Example 6.5-1: Diffusion of Hydrogen through Nafion

Nafion is a polymer manufactured by DuPont that is widely used as a selective membrane in polymer – electrolyte membrane fuel cells. The protons produced from the electrochemical reaction in the anode side of the fuel cell travel through the membrane to the cathode. The Nafion membrane must be humidified to facilitate the flow of protons through it. At a water uptake of 22 (molecules H_2O/molecules of sulfonic groups in the membrane), the concentration of protons in the membrane was estimated by Spry and Fayer [1] to be $0.54\frac{\text{mol}}{\text{L}}$. Determine the flux of protons through a membrane with a thickness of 0.175 mm. The diffusivity at a temperature of 30.5°C and a water uptake of 22 was estimated from data obtained by Ochi et al. to be $1.9\times10^{-9}\frac{\text{m}^2}{\text{s}}$ [2]. Assume that the reaction in the cathode chamber to form water is occurring instantaneously.

Strategy

We can use the diffusive flux equation to calculate the flow of protons through the membrane in the fuel cell.

Solution

The equation for diffusive flux is given by:

$$N_A = \underline{\hspace{6cm}}$$

Since the problem is stating that the reaction on the cathode chamber is occurring instantaneously, we can assume the concentration $C_{A_2} = \underline{\hspace{2.5cm}}$.

We can now calculate the flux by substituting the concentrations, thickness of the membrane and proton diffusivity into the equation shown above, as shown in the following steps:

$$N_A = \frac{\underline{\hspace{4cm}}\frac{\text{m}^2}{\text{s}}\left(\underline{\hspace{2.5cm}}\frac{\text{mol}}{\text{L}} - \underline{\hspace{2.5cm}}\right)\left(\frac{\underline{\hspace{2.5cm}}}{\underline{\hspace{2.5cm}}}\right)}{(\underline{\hspace{2.5cm}}\ \text{mm})\left(\frac{1\ \text{m}}{1000\ \text{mm}}\right)}$$

$$\boxed{N_A = \underline{\hspace{4cm}}\frac{\text{mol}}{\text{m}^2\cdot\text{s}}}$$

1. Spry, D.B., Fayer, M.D., *Journal of Physical Chemistry B*, 113, 10210 – 10221 (2009)

2. Ochi, S., Kamishima, O., Mizusaki, J., Kawamura, J., *Solid State Ionics*, 180, 580 – 584 (2009)

Example 6.5-3: Diffusion of Oxygen through Gas – Diffusion Layer

The oxygen in the cathode side of a proton – exchange membrane fuel cell diffuses to the catalyst layer through a gas – diffusion layer (GDL). The GDL has a thickness of 100 µm, and is typically made of a porous material which may be fabricated with either carbon cloth or carbon paper. The GDL has a porosity of 0.5 and a tortuosity of 1.63 [3]. Determine the flux of oxygen through the GDL if its partial pressure is 98.96 kPa and the operating temperature of the fuel cell is 50 °C. Assume there is steam in the pores of the GDL and that the reaction in the catalyst layer in occurring instantaneously.

Strategy

The equation defining diffusive flux in porous solids will be used to calculate the flux of oxygen through the GDL.

Solution

Section 6.5C of Geankoplis gives the equation for steady state flux in a porous media:

$$N_A = \rule{5cm}{0.4pt}$$

The diffusivity D_{AB} can be obtained using the Fuller method from Section 6.2E of Geankoplis to be:

$$D_{AB} = \rule{5cm}{0.4pt}\ \frac{\text{m}^2}{\text{s}}$$

The concentrations of oxygen can be obtained from the ideal gas law, as shown below:

$$C_{A_1} = \frac{\rule{2.5cm}{0.4pt}\ \text{kPa}}{\left(\rule{2.5cm}{0.4pt}\ \frac{\text{kPa}\cdot\text{m}^3}{\text{kgmol}\cdot\text{K}}\right)\left(\rule{2.5cm}{0.4pt}\ \text{K}\right)}$$

$$C_{A_1} = \rule{3cm}{0.4pt}\ \frac{\text{kgmol}}{\text{m}^3}$$

Since we are assuming the reaction in the cathode is occurring instantaneously, the concentration of oxygen at the catalyst layer will be $C_{A_2} = 0$

3. Hao, L., Cheng, P., *Journal of Power Sources*, 186, 104–114 (2009)

Now we can substitute the corresponding values into the equation for diffusive flux to get:

$$N_A = \frac{\_\_\_\_\_\_\_\_\left(3.04\times10^{-5}\,\frac{m^2}{s}\right)\left(\_\_\_\_\_\_\_\_\,\frac{kgmol}{m^3}\right)}{\_\_\_\_\_\_\_\_\left(\_\_\_\_\_\_\_\_\,\mu m\right)\left(\frac{\qquad}{}\right)}$$

$$\boxed{N_A = \_\_\_\_\_\_\_\_\_\_\_\_\,\frac{kgmol}{m^2\cdot s}}$$